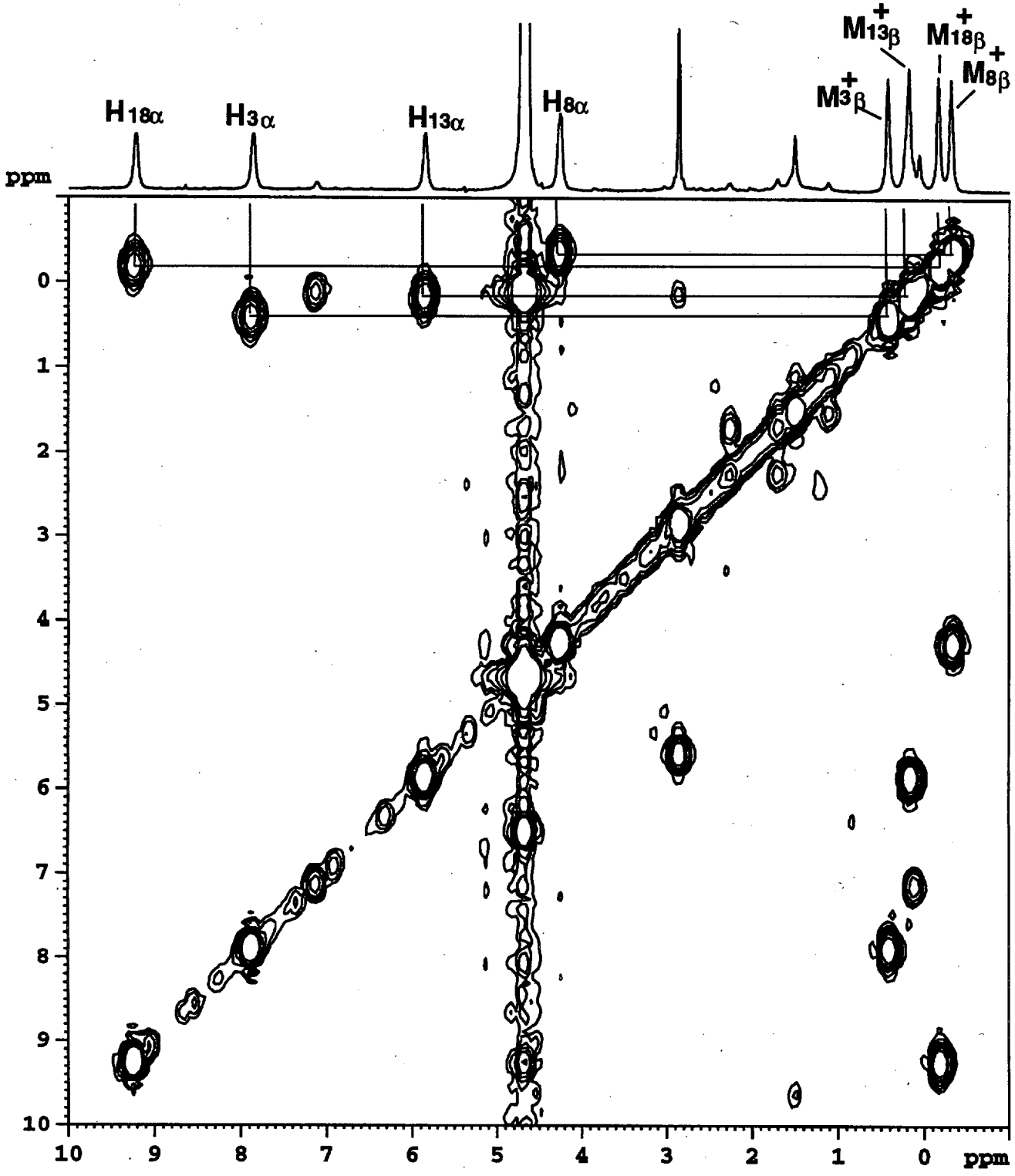

Figure 1S: Portion of the 400 MHz ^{1}H NMR COSY spectrum of ~3 mM [hemin **3**]CN_2^{-1} in 2:1 v:v $(C^2H_3)_2SO$:^2H_2O at 25°C illustrating the scalar connectivities involving the four pyrrole ethyl groups.

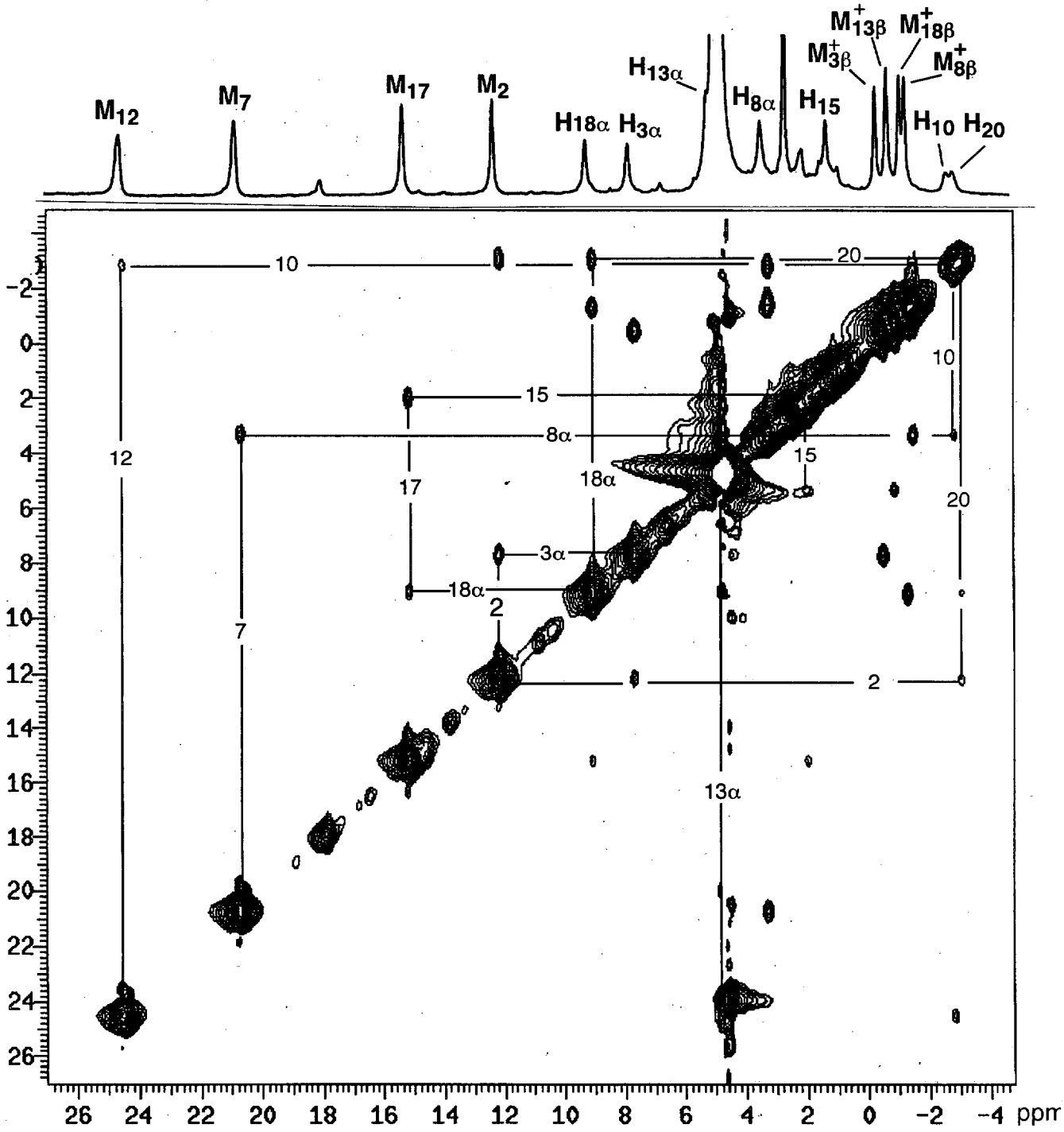

Figure 2S: 400 MHz ^{1}H NMR NOESY spectrum (mixing time 60 ms) of ~3 mM [hemin **3**]CN_2^{-1} in 2:1 v:v $(C^2H_3)_2SO_2$:^2H_2O at -20°C That illustrates the dipolar contacts about the heme periphery which uniquely identify each signal. Peak labeling is given according to structure **3**, with Mq (methyl) and Hq (single protons) at position q.

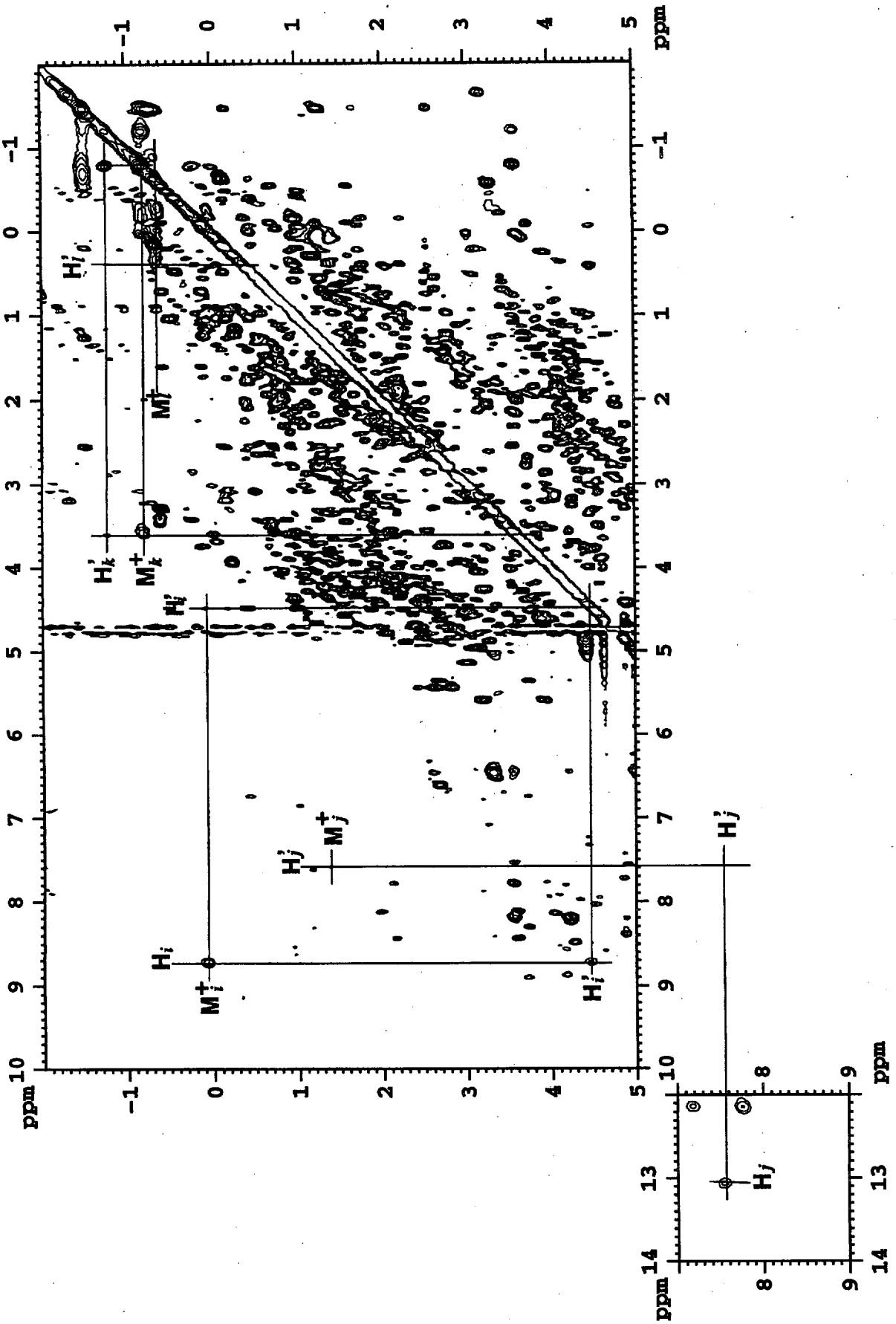

Figure 3S: Portion of the 600 MHz ^{1}H NMR TOCSY spectrum (mixing time 30 ms) of ~3 mM metMb(**3**)CN in ^2H_2O, 50 mM phosphate, 100 mM NaCl, 10 mM KCN at pH 8.2 at 25°C, illustrating the scalar contact for three of the four heme ethyl groups. The fourth heme ethyl protons for pyrrole ring *l* are too dispersed (~12 ppm) to allow effective spin-locking. The necessary NOESY cross peaks, however, are observed in Figure 4S.

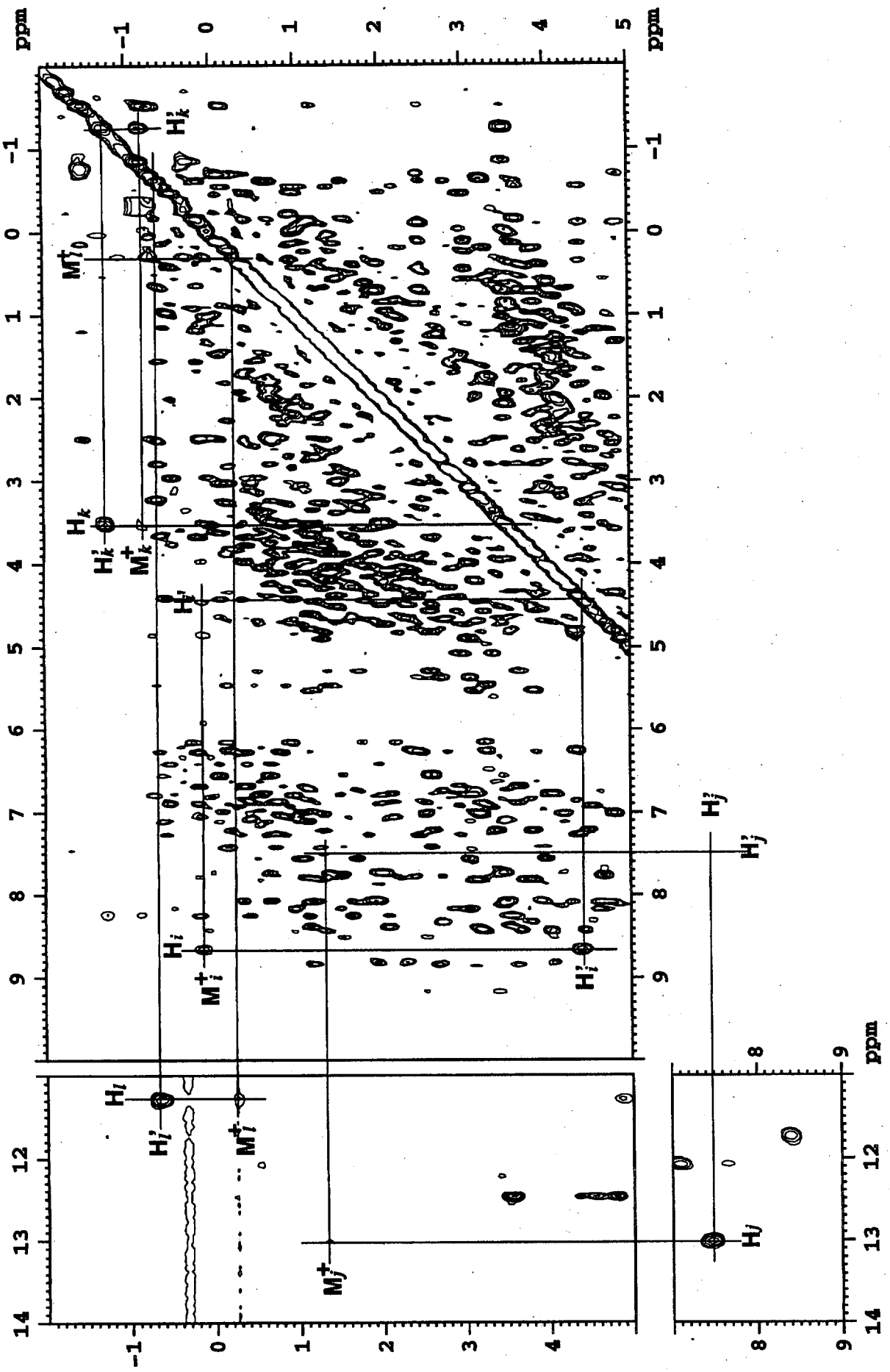

Figure 4S: Portions of the 600 MHz ^{1}H NMR NOESY spectra (60 ms mixing time) of ~3 mM metMb(3)CN in ^2H_2O, 50 mM phosphate, 100 mM NaCl, 10 mM KCN at pH 8.2 at 25°C, illustrating the dipolar contact for the four heme ethyl groups.